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13 October 1989
PSH:89:106L

Office of Naval Research
Department of the Navy
800 N. Quincy Street
Arlington, Virginia 22217-5000

Attention: Dr. R. Shwartz
Scientific Officer
DODAAD Code N00014

Subject: Contract No. N00014-87-C-0251

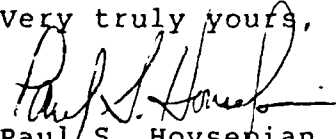
Reference: CLIN 0002, CDRL Sequence A001

Dear Sir:

In accordance with the requirements of the subject contract, enclosed is Raytheon Research Division's Progress Report. This report reflects the effort performed under the subject contract for the period 1 October 1988 - 30 September 1989.

If you have any questions, please contact the writer at (617) 860-3131.

Very truly yours,


Paul S. Hovsepian
Contracts Manager

cc: ACO, DODAAD Code S2205A
Director, Naval Research Laboratory
Attn: Code 2627
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FY89 End of Fiscal Year Letter
(01 Oct 1988 - 30 Sept 1989)

ONR CONTRACT INFORMATION

Contract Title : High Modulus Coatings
Performing Organization : Raytheon Company
Principal Investigator : Randal W. Tustison
Contract Number : 87-C-0251
R&T Project Number: 431a017

ONR Scientific Officer : Dr. Robert Schwartz

Accession For	
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HIGH MODULUS COATINGS

N00014-87-C-0251

Research Goals:

Explore methods and mechanisms by which the ultimate fracture strength of ZnS can be increased without degrading its optical transparency in the bandpass of interest.

Results:

In 1988 we demonstrated that relatively thin films of Y₂O₃ could be used to strengthen substrates of ZnS. The observed strengthening effect was shown to be related to the intrinsic compressive stresses in the film. During the past year additional experiments have shown that the magnitude of the strengthening is relatively independent of film thickness, deposition method (i.e. magnetron vs. ion beam sputtering) and even film composition, depending only on the sign of the film stress. For example, the strengthening effect was not observed in ZnS samples coated with evaporated YF₃ films, wherein the intrinsic film stresses were found to be tensile. Ion assisted evaporation of the same material resulted in the creation of net compressive stresses and the substrate strengthening effect was again observed. In all cases the observed effect was found to be a 25-35% increase which is in agreement with a model proposed by Marion (1) wherein flaws originally residing at the surface of a brittle material like ZnS are internalized.

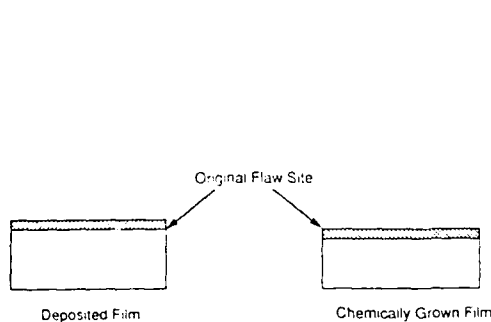
Alternatively, Green(2) has shown that much larger increases in fracture strength can occur if the pre-existent flaws are encompassed within the compressive strain field. To this end, we have explored the use of solid state reacted or diffused coatings in an effort to form such compressed surface regions. Analysis by Mecholsky(3) indicates that the critical surface flaws in ZnS are on the order of 100 microns. This would imply that the compressed regions would have to extend at least to this depth within the sample for large strengthening effects to be observed.

We have succeeded in forming altered surface regions to depths of up to 0.5 mm in ZnS samples by diffusion and reaction of transition metals like Cr, Mn, Fe, Ni and Co. The concept of the solid state diffused coating is illustrated in Figure 1a. Figure 1b illustrates the depth of the transformed region, indicated by the grain growth which occurred exclusively in the diffused region. The extent of this grain coarsening depends directly on the concentration of the transition metal. Preliminary results indicate that compressive surfaces were formed for several of the diffused species. Hardness increases occurred in most cases with an increase in fracture toughness observed for Fe in ZnS. Corresponding strength increases, up to 50% for Fe, were also observed. We believe that this may be a very useful and unique method of tailoring the mechanical, optical and surface chemistry behavior of ZnS. Work should continue in this area.

From a mechanical properties viewpoint, diamond is the ultimate IR material. Although the growth of diamond films by CVD processes is under development at many laboratories throughout the country, very little effort has been expended on the mechanical characterization of the resulting polycrystalline diamond films. We have undertaken the development of a simple biaxial tension apparatus to evaluate the mechanical properties of CVD diamond. The apparatus is shown schematically in Figure 2. In this test, a liquid is injected into the test chamber, thereby pressurizing a membrane of the film material to be tested. The deflection of this membrane is sensed as a height change and a pressure vs height (displacement) curve is traced as shown in Figure 3. This data can then be related to the stress and corresponding strain in the film at the pole, or position of maximum displacement. Young's Modulus is one of the parameters which can be obtained from such an analysis, as illustrated in Figure 3 for a polycrystalline diamond film. Here, the elastic modulus was found to be 677 GPa. Work is continuing on the development of the test fixturing and absolute calibration of the test. Mechanical data taken for diamond films grown under various growth conditions will be available in the near future.

Finally, while monolithic diamond windows/domes would be ideal for many IR applications, diamond coatings on existing IR materials would also be of great value and potentially a more realistic near term goal. ZnS and ZnSe would be ideal broad band substrates for such deposition as well as Ge. However, diamond does not nucleate readily on any of these materials. We have investigated interlayers for diamond growth onto IR materials like ZnS, ZnSe and Ge. Successful interlayers must 1) nucleate diamond 2) promote adhesion of diamond to the substrate 3) be IR

transparent and in some cases 4) protect the substrate from chemical attack during diamond deposition. Interlayers investigated were, diamond-like (a-C:H) and hard carbon films, BN films and thin SiC films. All interlayer films were subjected to two sequences of thermal cycling prior to diamond nucleation experiments. The transmittance curves of four candidate interlayer films on silicon are shown in Figure 4 before and after thermal cycling. The IBED BN films were found to be completely inert to thermal cycling and did enhance diamond nucleation by 41x. The hard carbon film was found to be most effective at nucleating diamond on silicon, increasing the nucleation density by 365x, although the film appeared to be completely removed during the initial phase of diamond growth. Surface analysis suggested that the formation of a SiC layer is most responsible for this observation. Even for the case of SiC, certain orientations and in particular the (220) orientation was found to be most favorable for diamond nucleation and growth. It is expected that interlayers like those studied here will by necessity be used when depositing diamond on IR transparent substrates, where seeding is either not possible or does not provide sufficiently durable interfaces in severe environments, like high speed raindrop impact.



(a)

(b)

Figure 1. Solid State Diffused Coating

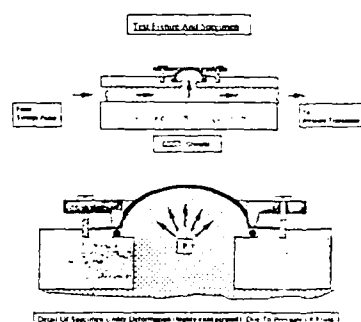


Figure 2. Biaxial Tension Test

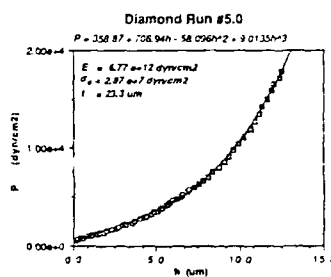


Figure 3. Pressure-Hgt. Curve

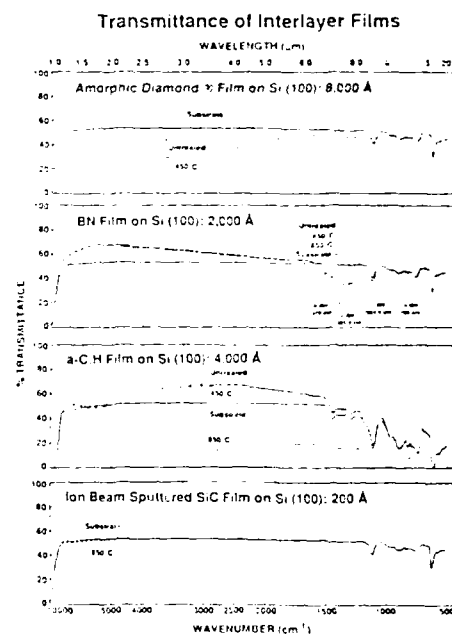


Figure 4. Transmittance Data

Future Plans:

- Characterize polycrystalline diamond films using the biaxial tension apparatus
- Deposit polycrystalline diamond films onto Ge samples (using interlayer as required) and test in a rain erosion test facility

References:

1. J.E. Marion, Proc. Topical Conf. on *Optics & Adverse Environments*, Sponsored by OSA, Feb. 11-12 (1987) p. 56
2. D.J. Green, J. Mat. Sci., **19**, 2165 (1984).
3. D.L. Yoder and J.J. Mecholsky, *Fractographic Analysis of CVD ZnS*, Report to ONR, May, 1988.

D. List of Publications/Reports/Presentations

1. Papers Published in Refereed Journals

R. W. Tustison, T. E. Varitimos, D. G. Montanari and J. M. Wahl
"Stress in Y_2O_3 Thin Films Deposited by Radio-Frequency Magnetron and in Beam Sputtering"
J. Vac. Sci. Technol., A7, 2256 (1989).

2. Non-Refereed Publications and Published Technical Reports

3. Presentations

a. Invited

b. Contributed

"Intermedita Layers for the Deposition of Polycrystalline Diamond Films" to be
presented at 36th National Symposium of Amer. Vac. Society, Boston, Oct. 25, 1989.

4. Books (and sections thereof)

Enclosure (2)

F. Program Participants:

- Randal W. Tustison (Principal Investigator)
Principal Scientist
- Joe Wahl
Scientist
- Dennis Montanari
Associate Scientist
- Charles Willingham
Principal Scientist
- Tom Hartnett
Senior Scientist
- Rick Miller
Scientist
- Greg Cardinale
Scientist

G. Other Sponsored Research:

None

E. LIST OF HONORS/AWARDS

Name of Person
Receiving Award

Recipient's
Institution

Name, Sponsor and Purpose of Award

- NONE -

Enclosure (3)

H. SUMMARY OF FY89
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/PARTICIPANTS
(Number Only)

Papers Submitted to Refereed Journals (and not yet published): (1)

Papers Published in Refereed Journals: (1)

Books (and sections thereof) Submitted for Publication:

Books (and sections thereof) Published:

Patents Filed:

Patents Granted:

Invited Presentations at Topical and Scientific/Technical Society
Conferences:

Contributed Presentations at Topical and Scientific/Technical Society
Conferences:

Honors/Awards/Prizes:

Non-Refereed Publications and Published Technical Reports:

Number of Graduate Students:

Number of Post Docs:

Enclosure (4)